

COPROCESSING COAL LIQUIDS WITH PETROLEUM RESID

Michael M. Schwartz and Albert L. Hensley

Amoco Oil Company
Amoco Research Center
P.O. Box 400
Mail Station H-4
Naperville, IL 60566

ABSTRACT

A series of bench-scale experiments was run to determine the advantages and disadvantages of processing coal liquids with petroleum resid. Standard resid, blends of resid containing 15 and 40% coal-derived liquids (from Wilsonville), plus the neat coal-derived component of the blends were evaluated. The parameters evaluated were: (1) Hydrogen Consumption; (2) Conversions (1000+°F, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and Ramsicarbon removal (HDR)); (3) Catalyst Activity; (4) Unit Operability; and (5) Product Quality (total liquid product plus 360-, 360-650, 650-1000, and 1000+°F fractions).

The major findings are: (1) Hydrogen consumption and HDN increased with increasing coal liquids but HDS and HDR were independent of feed; (2) Coal liquids did not accelerate catalyst deactivation; (3) Unit operability increased with increasing coal-liquids content of the feed; (4) Aromaticity of the 360-, 360-650, and 650-1000°F fractions all increased with increasing coal liquids.

INTRODUCTION

As part of its synfuels development program, Amoco has been doing research to improve the economics of converting coal into liquid fuels using the technique known as direct coal liquefaction.⁽¹⁻³⁾ Direct liquefaction is a proven technology--used by Germany to produce liquid fuels during World War II. However, it is not economic at the current price of crude oil and there is no current commercial source of coal liquids. The economics of coal liquefaction would improve if existing petroleum refinery units could be used to upgrade coal-derived liquids rather than building a grass-roots facility. The research program described herein was conducted to determine the advantages and disadvantages of processing coal liquids with petroleum resids.

EXPERIMENTAL

Feedstocks

Maya-containing 1000+°F resid blend (Feed A) was chosen as the resid benchmark. Coal-derived liquid (containing about 50% 1000+°F material and designated Feed B) obtained from the Wilsonville, Alabama pilot plant was used to make the blends. The feedstocks containing 15% and 40% coal liquids were designated Feed C and Feed D respectively. The inspections of these feeds are shown in Table I.

Reactor

An automated continuous resid hydroprocessing pilot plant was used. High pressure hydrogen enters through a pressure stepdown and metering device and exits through an outlet pressure control loop so that hydrogen pressure and flow can be controlled within narrow limits. The existing gases pass either into a gas sampling device or through a scrubber and into a wet test meter. Feed is added by a positive displacement pump. Feed and hydrogen flow concurrently upflow through a vertical pipe reactor. The pipe reactor is heated by four independently fired and controlled heating zones. Reactor temperature is measured in a centrally located axial thermocouple well by a travelling thermocouple. Feed exits from the top of the reactor and is collected in either of the following two ways:

1. In normal operation, feed exits through a high pressure gas-liquid separator via a Research Control Valve (RCV) with a control loop that maintains a constant liquid level in the high pressure separator. In this mode, product liquid is collected continuously in a glass bottle at atmospheric pressure.
2. Under some process conditions, solids are formed which plug the RCV making the unit inoperable in that mode. The high pressure receiver is used when high solids conditions are encountered. In this mode, product liquid is held in a heated (about 300°F) Hoke vessel at the system pressure until the vessel is drained and the product is collected (typically every 24 hours).

Reaction Conditions and Sequence of Feedstock Testing

Only feedstock and reactor temperature were varied. Kept constant were liquid feedrate, pressure, and hydrogen flow rate. The feedstock comparison started with a reactor temperature of "base". Sequentially, data were obtained with Feedstocks A (0% coal-liquids), C (15% coal liquids), D (40% coal-liquids), and then with A (0% coal-liquids) again to determine catalyst deactivation. The temperature was then raised to "base + 20°F" continuing with Feedstock A (0% coal-liquids) and then sequentially testing as was done at "base". At the end of the "base + 20°F" test sequence, the program was expanded to also test the 100% coal-liquids feed, Feed B. This experimental program was designated Run 17-258.

RESULTS

Table II shows the average total liquid product inspections for each feedstock in the sequential order the feeds were run; the standard deviation for each inspection is given in parenthesis. The inspections listed in Table II are: °API, percent Shell hot filtration (SHFT), percent hexane insoluble; also percents sulfur, nitrogen, and Ramsarbon.

Table III shows the mass balance data: percent C₁-C₄ gas-make, total hydrogen consumption (SCF/B) and weight percent product recovered.⁴ Table IV shows the conversions obtained with each feed, again in the sequential reaction order. Sulfur, nitrogen, and Ramsarbon conversions are the averages for the run period.

Inspections on the 360-, 360-650, 650-1000, and 1000+°F fractions (collected by atmospheric distillation of the 650-°F fractions and vacuum distillation of the 650+°F material) have been obtained for each of the feedstocks after reaction at each

temperature. The data from reaction at "base" and "base + 20°F" are shown in Tables V and VI respectively.

Unit Operability

Figure 1 shows the effect of coal-liquids and reaction temperature on SHFT during normal operation through the RCV. Our data clearly show that operability increases with increasing coal-liquids content and the improved operability with added coal liquids is much more pronounced at the higher temperature.

In normal operation, the reaction product continually exits the unit through a separator, the level of which is controlled by a research control valve (RCV). During periods of good operability, flow through the RCV is smooth and the liquid product has a low value for an inspection called the Shell Hot Filtration Test (SHFT). SHFT is a measure of the amount of solids formed. At "base temperature" operation through the RCV was possible with either 0, 15, or 40% coal-liquids giving average SHFT inspections of about 1.2, 0.8, and 0.6, respectively. At "base + 20°F" operability was fine with 15, 40 and 100% coal-liquids resulting in SHFT inspections of 0.8, 0.5, and 0.2, respectively.

In contrast, operation at "base + 20°F" with Feed A was impossible; the RCV plugged and had to be by-passed by using the high pressure receiver. The SHFT inspections of these high pressure receiver products, about 0.88, are lower than the SHFT of 1.2 obtained at "base". Since operability should improve with lower SHFT inspections, the SHFT data obtained from operation with the high pressure separator do not accurately reflect unit operability and cannot be compared with data obtained during operation through the RCV. We do not know why the SHFT inspections are not comparable.

Catalyst Activity

The use of coal liquid-containing feeds had no unusual effect on catalyst activities. Catalyst activity only declined with time on stream at a given temperature, with deactivation increasing with increasing temperature, as would be expected for any feed.

The data for denitrogenation have the lowest experimental error and are used to show our results, but similar trends were followed for sulfur and Ramscarbon reduction.

Figure 2 shows the relative denitrogenation reactivity for each of the feeds in the sequential order which they were run. Relative reactivity is defined as the ratio of 1st-order rate constants to Day 69 for reaction at base and the ratio to day 105 for reaction at "base + 20°F". As is seen, the reactivity of benchmark Feedstock A at "base" was identical before and after running the coal-liquid blends. The reactivity at "base + 20°F" was slightly lower after running the blends, but the decline was very small and is attributed to the expected catalyst deactivation at this temperature and not to the use of coal liquid-containing feeds.

The explanation for the greater denitrogenation of the coal liquids-containing feeds is unknown. One possibility is that the nitrogen-containing compounds in the coal liquids are inherently easier to denitrogenate than those in the petroleum resid. Alternatively, the greater denitrogenation of the coal liquids-containing feeds might simply be a result of their greater amounts of 1000-°F material present (14, 25, and

50% in Feeds C, D, and B, respectively, versus 8% in A); previous studies have shown that ease of upgrading increases as boiling point of the feed decreases.

Conversions and Hydrogen Uptake

The percent conversions of 1000+°F material to 1000-°F material, nitrogen removal, Ramscarbon removal, and sulfur removal for each coal liquid-containing feed plus Feed A at "base" and "base + 20°F" are shown in Figures 3-6 respectively. Conversion of 1000+°F material is calculated (correcting for 1000-°F material in the feed) from one actual distillation of combined product collected over each run period. Nitrogen, Ramscarbon, and sulfur conversions are calculated from inspections of daily products and then averaging the results. Hydrogen uptake is shown in Figure 7. Hydrogen uptake is the average of mass balance calculations taken during each run period.

All conversions with the 15 and 40% blends of coal liquids were always equal to or greater than the conversion with Feed A alone, indicating that no penalty in conversion would result from the addition of coal liquids. Also, the 1000+°F conversions of the blends were higher than those of the straight A and B feeds. This suggests the possibility of a synergistic interaction, but the data do not warrant a definitive statement to that effect. C₁-C₄ gas make appeared independent of feed at each temperature.

Denitrogenation increased with increasing coal-liquids. However, as discussed above, this could have simply been caused by the lower boiling points of these feeds.

Ramscarbon and sulfur conversions were slightly higher at each temperature with the blends than with Feed A, but the differences probably are not statistically significant.

Hydrogen uptake increased with increasing coal liquids at each temperature and hydrogen uptake increased with increasing temperature. This result is expected because the coal liquids are more aromatic than petroleum resid (Feed A) and more hydrogen would go into ring saturation.

Product Quality

Each boiling range fraction got more aromatic and had a lower sulfur content with increasing coal-liquids content at each temperature. These results are illustrated in Figures 8 and 9 which show percent aromatics and percent sulfur in the 650-1000°F cuts, respectively.

The nitrogen contents of the cuts did not show a consistent pattern. The 360-°F cut showed increasing nitrogen with increasing coal-liquids. The 360-650°F fraction showed increasing nitrogen with increasing coal-liquids only at "base". The nitrogen content within the 650-1000°F fraction was the same with each feed at each reaction temperature.

SUMMARY

The purpose of these experiments was to answer the question: "How would the addition of coal-liquids affect resid hydroprocessing?", specifically addressing the

topics of unit operability, conversion and hydrogen consumption, catalyst activity maintenance, and product quality.

Our conclusions are:

1. Unit Operability: BETTER
2. Conversions: EQUAL OR HIGHER
3. Hydrogen Consumption: HIGHER
4. Unexpected Effect on Catalyst Activity: NONE
5. Product Quality: MORE AROMATIC, LOWER SULFUR.

REFERENCES

1. Brooks, J. A., R. J. Bertolacini, L. C. Gutberlet, and D. K. Kim, "Catalyst Development for Coal Liquefaction," EPRI Final Report for RP #408-1, -2, November 1979.
2. Mahoney, J. A., J. J. Helstrom, and R. J. Pellet, "Coal Liquefaction Catalyst Development," DOE Final Report for Contract #DE AC 22-79ET-14803, August 1982.
3. Tait, A. M., M. M. Schwartz, and M. A. Pacheco, "Advanced Coal Liquefaction Catalyst Development, DOE Contract Number DE-AC22-81PC40009: Final Report," April 29, 1986.

TABLE I
FEEDSTOCK INSPECTIONS

Percent Coal				
Liquids:	0	15	40	100
Feedstock				
Identification:	<u>A</u>	<u>C (a)</u>	<u>D (b)</u>	<u>B (c)</u>
Elemental Analyses				
C, %	84.85	85.38	86.22	88.40
H, %	10.39	10.06	9.55	8.48
S, %	4.04	3.38	2.56	0.26
O, %	1.48	0.83	2.01	1.57
N, %	0.49	0.54	0.59	0.78
Ni, ppm	56	46	34	<2
V, ppm	246	201	152	<2
Ramscarbon, %	18.5	20.1	20.6	22.4
Oil, %	29.3	29.2	29.2	24.8
Resin, %	58.5	56.9	56.5	56.1
Asphaltene, %	12.0	11.5	9.4	4.3
°API	6.8	6.0	4.0	-1.5
% 1000+°F (d)	92	85.6	75	49.5

(a) C = 85% A + 15% B.

(b) D = 60% A + 40% B.

(c) Blend of Wilsonville liquids derived from Illinois No. 6 coal.

(d) By distillation.

TABLE II
RUN 17-258
AVERAGE TOTAL LIQUID PRODUCT INSPECTIONS*

Reaction Temperature	Base				Base + 20°F				
Feedstock Identification	A	C	D	A	A	C	D	A	B
% Coal Liquids in Feed	0	15	40	0	0	15	40	0	100
Sample Days	62-69	72-77	80-84	87-96	99-105	110-119	123-132	136-142	146-152
°API	21.9 (.43)	19.0 (.1)	16.6 (.2)	21.2 (.5)	25.5 (.6)	23.2 (.5)	20.2 (1.0)	25.6 (.5)	10.3 (.4)
S, wt%	0.62 (.03)	0.47 (.05)	0.27 (.01)	0.60 (.03)	0.40 (.04)	0.34 (.02)	0.25 (.04)	0.52 (.04)	0.080 (.027)
N, wt%	0.323 (.025)	0.348 (.031)	0.331 (.015)	0.321 (.016)	0.266 (.023)	0.294 (.013)	0.288 (.025)	0.285 (.010)	0.304 (.014)
Ramscarbon, wt%	7.05 (.04)	7.26 (.30)	6.78 (.18)	7.15 (.15)	3.20 (1.37)	3.02 (1.26)	3.56 (1.11)	4.34 (1.04)	4.66 (.13)
SHFT	1.07 (.52)	0.80 (.35)	0.61 (.30)	1.30 (.31)	0.97 ^(a) (.46)	0.83 (.23)	0.48 (.13)	0.78 ^(a) (.22)	0.15 (.05)
Hexane Insoluble, wt%	3.94 (.35)	4.18 (.55)	3.26 (.14)	4.18 (.27)	2.60 (.61)	2.61 (.24)	2.16 (.21)	2.63 (.12)	1.67 (.2)

*Mean (Standard Deviation)

(a) Sample from high-pressure receiver.

TABLE III
RUN 17-258
MASS BALANCE DATA

Reaction Temperature	Base				Base + 20°F													
Feedstock Identification	A		C		D		A		A		C		D		A		B	
% Coal Liquids in Feed	0		15		40		0		0		15		40		0		100	
Sample Days	68	72	77	83	92	104	117	131	139	142	147	152						
C ₁ -C ₄ , %	3.1	3.7	3.8	3.8	4.0	10.0	6.2	5.0	6.0	6.0	7.5	7.5						
Hydrogen Consumption, SCF/B	1078	1139	1226	1456	1105	1858	1620	1660	1338	1468	1837	1754						
Wt% Product Recovered	100	90	100	97	86	114	101	96	96	100	99	99						

TABLE IV
RUN 17-258
CONVERSIONS

Reaction Temperature	Base			Base + 20°F							
Feedstock Identification	A	C	D	A	A	C	D	A	B		
% Coal Liquids in Feed	0	15	40	0	0	15	40	0	100		
Sample Days	62-69	72-77	80-84	87-96	99-105	110-119	123-132	136-142	146-152		
% Desulfurization	85	86	89	85	90	90	90	88	69		
% Denitrogenation	32	35	44	32	44	46	51	42	62		
% Ramsarbon Conv.	62	64	67	62	83	85	82	77	79		
% 1000°+ Conv. by Distillation	—	70.0	71.1	67.5	82.7	88.8	88.9	82.4	77.4		

TABLE V
INSPECTIONS OF PRODUCTS AFTER "BASE" HYDROTREATING

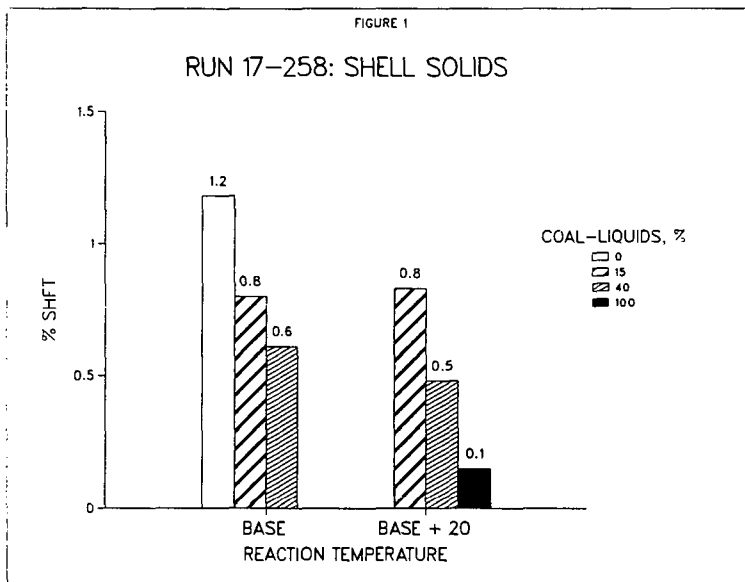
Coal Liquids in Feed, %	0	15	40
Feedstock Identification	A	C	D
Run Identification, 17-258-	94	77	84
<u>360°F-, wt%</u>	4.8	4.1	3.9
C, %	82.61	86.04	86.26
H, %	13.95	14.17	14.01
N, ppm	20	212	241
S, %	0.079	0.049	0.022
Paraffins, wt%	54.8	48.0	44.2
Cycloparaffins, wt%	29.0	31.6	34.4
Aromatics, wt%	16.3	20.4	21.4
<u>360-650°F, wt%</u>	24.9	27.7	30.7
C, %	87.25	87.65	87.84
H, %	12.97	12.56	12.07
N, ppm	832	1220	1310
S, %	0.74	0.056	0.034
°API	31.0	30.3	26.6
Paraffins, wt% ^(a)	30.6	25.3	18.1
Cycloparaffins, wt% ^(a)	30.5	31.0	31.1
Aromatics, wt% ^(a)	38.9	43.7	50.8
C-sub-A, wt% ^(a)	17.2	17.5	23.1
<u>650-1000°F, wt%</u>	37.9	41.5	43.1
C, %	87.48	87.74	88.85
H, %	11.81	11.23	10.87
N, ppm	0.30	0.28	0.32
S, %	0.51	0.41	0.22
°API	19.68	16.53	13.30
Ramscarbon, %	7.30	7.61	5.75
Paraffins, wt% ^(a)	14.5	12.5	7.8
Cycloparaffins, wt% ^(a)	31.2	29.5	22.0
Aromatics, wt% ^(a)	54.3	58.0	70.2
C-sub-A, wt% ^(a)	25.8	30.6	35.8
Oils, %	70.3	65.1	58.3
Resins, %	28.7	33.0	39.8
Asphaltenes, %	0	0	0
<u>1000°F+, wt%</u>	29.9	25.7	21.7
C, %	87.89	88.38	89.13
H, %	9.96	9.61	9.08
N, ppm	0.61	0.65	0.64
Ni, ppm	22	25	20
V, ppm	6	5	2
S, %	1.18	1.00	0.66
°API	5.24	2.79	0.12
Ramscarbon, %	23.7	29.1	31.6

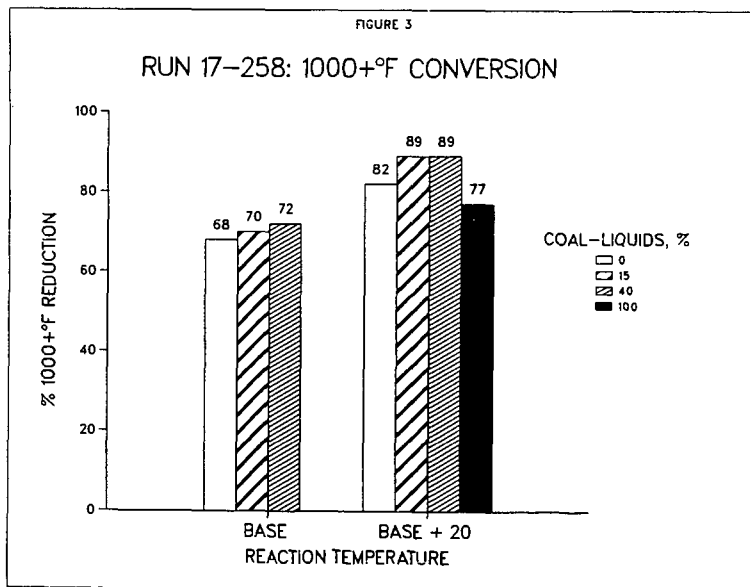
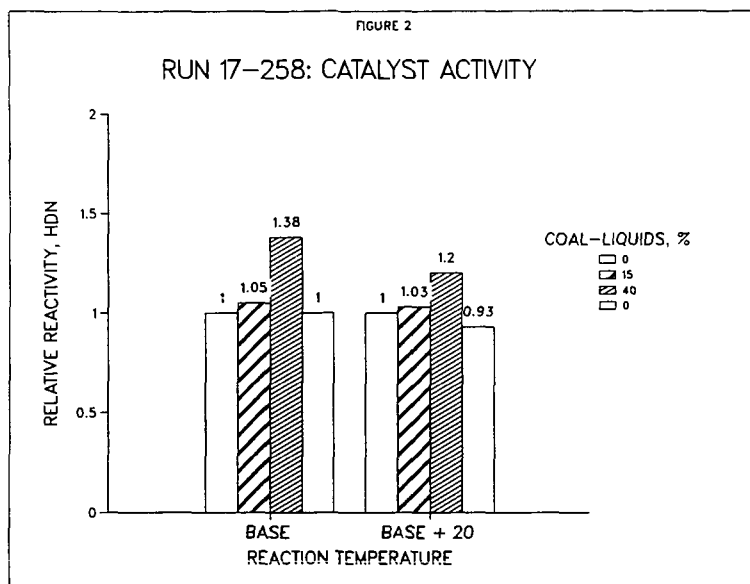
(a) By Robinson-type mass spectral analysis.

TABLE VI
DISTILLED PRODUCT INSPECTIONS FROM
HYDROTREATING AT "BASE + 20°F"

Feed Identification: Run 17-258-	A 135-139	C 111-116	D 122-126	B 148-151
Coal Liquids in Feed %:	0	15	40	100
<u>360°F-Wt%</u>	9.08	9.0	8.5	5.1
C, %	85.07	81.73	85.32	86.87
H, %	14.41	13.35	14.09	13.17
N, ppm	136	158	222	348
S, ppm	480	238	300	279
<u>360-650°F Wt%</u>	39.51	37.7	38.2	46.0
C, %	86.94	87.19	87.89	88.89
H, %	12.64	12.47	12.11	10.86
N, %	0.132	0.124	0.115	0.137
S, ppm	1250	440	240	50
°API	32.7	32.6	28.4	19.0
Paraffins, wt% ^(a)	30.2	27.7	21.7	4.8
Cycloparaffins, wt% ^(a)	30.7	30.4	30.9	28.8
Aromatics, wt% ^(a)	39.1	41.9	47.4	66.4
C-sub-A, wt% ^(a)	18.0	17.2	20.1	32.4
<u>650-1000°F, Wt%</u>	33.77	43.4	43.9	36.2
C, %	87.33	88.26	88.90	91.14
H, %	11.28	10.65	10.35	8.00
N, %	0.349	0.394	.337	.440
S, %	0.56	0.44	0.276	0.011
API	19.1	13.2	10.7	-1.2
Ramscarbon, %	1.2	2.5	1.8	1.1
Paraffins, wt% ^(a)	15.5	10.8	7.0	--
Cycloparaffins, wt% ^(a)	27.5	22.6	16.7	--
Aromatics, wt% ^(a)	57.0	66.6	76.3	100
C-sub-A, wt% ^(a)	28.8	33.8	41.7	63.1
Oils, %	68.0	61.3	55.9	35.1
Resins, %	31.1	35.7	41.1	62.6
Asphaltenes, %	0.4	0.8	0.4	0.8
<u>1000°F+, Wt%</u>	16.24	9.6	8.3	11.21
C, %	88.23	90.32	89.11	92.25
H, %	8.63	7.91	7.81	6.36
N, %	0.793	0.814	0.592	.206 ^(?)
S, %	1.39	.98	.63	.044
Ni, ppm	31	29	26	16
V, ppm	16	7	4	5
°API	-1.5	-5.6	-9.4	-11.4
Ramscarbon, %	34.7	42.5	52.5	49.9

(a) By Robinson-type mass spectral analysis





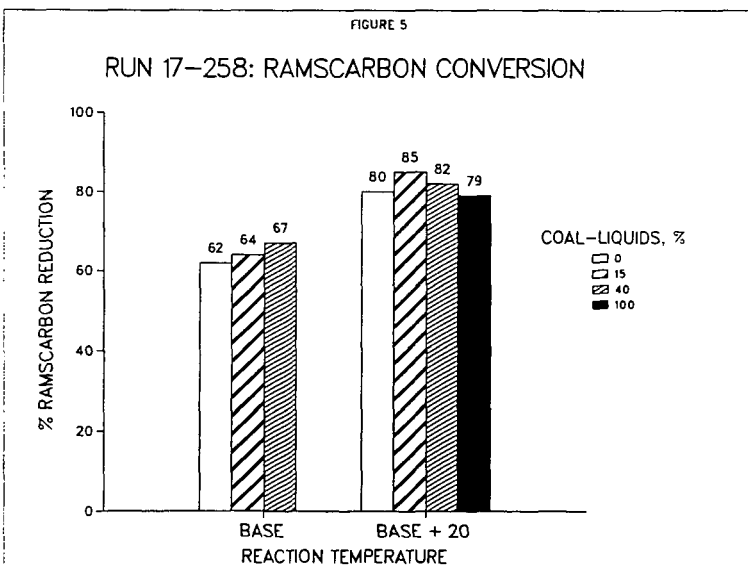
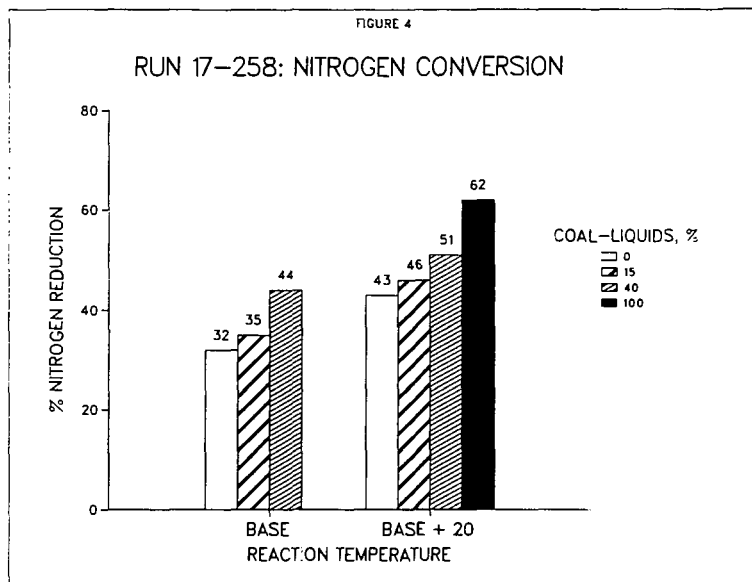


FIGURE 6

RUN 17-258: SULFUR CONVERSION

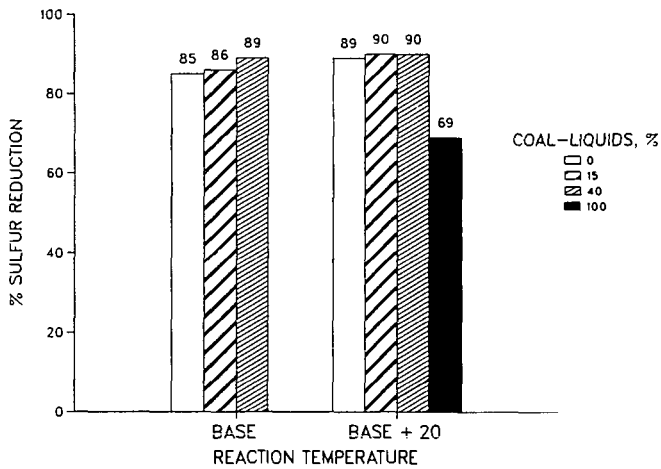


FIGURE 7

RUN 17-258: HYDROGEN UPTAKE

